

Supplementary Information

Ultra-Permeable Polyamide Membranes Harvested by Covalent Organic Framework Nanofiber Scaffolds: A Two-in-One Strategy

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Experimental details

Materials. 1,3,5-triformylphloroglucinol (Tp, 95%) was purchased from TongChuangYuan Pharmaceutical. Triaminoguanidinium chloride (TG_{Cl}) was synthesized according to the literature.²⁹ Trimesoyl chloride (TMC, 98%), anhydrous piperazine (PIP, 99%) were obtained from Sigma-Aldrich and Aladdin, respectively. Solvents and other reagents are commercially obtained and all chemicals were used without further purification. PES macroporous substrates with the diameter of 50 mm and the mean pore size of 0.1 μm were purchased from Haiyan Xindongfang Plastic Chemical Corporation. Deionized water (DI water, Wahaha) was used throughout this work.

Synthesis of Triaminoguanidinium chloride (TG_{Cl}): As shown in Fig. S1, 1.91 g of guanidine hydrochloride (Aladdin, 99%) and 10 mL 1,4-dioxane were added into a 50 mL round-bottom flask, respectively. 3.41 g of Hydrazine hydrate (Aladdin, 98%) was then added, and the mixture was refluxed under stirring condition for 2 h. The final product was isolated, washed with 1,4-dioxane and water, and dried under vacuum at 60 °C for 24 h to afford the white powder.

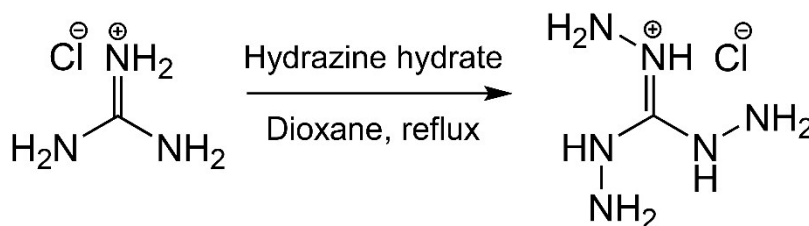


Fig. S1 Synthetic scheme of TG_{Cl}.

Synthesis of COF nanofibers. COF TpTG_{Cl} was synthesized based on the report by Banerjee and co-workers with several modifications.²⁹ It is synthesized via a Schiff base condensation between Tp and TG_{Cl} in 1,4-dioxane and water under the conventional solvothermal condition without any catalyst. Briefly, 0.2 mmol Tp (42 mg) and 0.2 mmol TG_{Cl} (28 mg) were added into a Teflon-lined stainless-steel autoclave (maximum capacity of 25 mL). Afterwards, the solvent of 1,4-dioxane and DI water (5:5 mL) was added, respectively. The mixture was then sonicated for about 10 min for well dispersing the monomers. The autoclave was sealed and kept at 120 °C for 72 h. The resultant product was isolated, washed with acetone and water, and dried under vacuum at 120 °C for 24 h to afford the dark-brown powder.

Construction of COF scaffold layers. Prior to the construction procedure, the COF nanofiber dispersion was firstly prepared. Generally, the obtained COF powder (150 mg) was added into water (500 mL), followed by a probe-sonication (600 W, 3 h) treatment. Next, the mixture was centrifuged at 8000 rpm for 15 min, and the collected supernatant was used as the final COF dispersion with the concentration about 0.008 mg mL⁻¹.

The COF scaffold layer was constructed by a vacuum filtration method. We used various dosages of COF dispersion for preparing the COF-deposited PES substrates with different COF deposition densities of 0, 0.019, 0.038, and 0.051 mg cm⁻², respectively. Typically, the COF dispersion was filtrated through the PES substrate under a negative pressure of 0.2 bar. After that, the COF-deposited PES substrates were heated at 60 °C for 30 min and stored in a desiccator for further use. The COF-deposited PES substrates prepared from the COF deposition density of 0.038 mg cm⁻² were used for next characterization.

Interfacial polymerization. Interfacial polymerization was implemented at ambient conditions. In brief, The COF-deposited PES substrate was horizontally placed on the glass plate, and 3 mL 0.05% (w/v) aqueous solution (PIP in water) was dropped onto the substrate surface and maintained for 30 s. Then, the aqueous solution on the membrane surface was drained and dried under ventilated conditions until no residual PIP solution was visible. 3 mL 0.05% (w/v) organic solution (TMC in *n*-hexane) was then poured onto the upper surface of PIP solution filled COF-deposited PES substrate for IP lasting for 2 min. Afterward, the organic solution was removed, and the membrane was cured at 60°C for 30 min. The resultant PA composite membrane was stored in water for use. The PA composite membranes prepared from the COF-deposited PES substrates with the COF deposition density of 0.038 mg cm⁻² were applied for subsequent characterization and NF tests. For comparison, the control membranes were prepared by the same IP procedure on the PES substrates without the COF layer.

Characterizations. Fourier transform infrared (FT-IR) spectra of samples were recorded on a Nicolet 8700 spectrometer (Thermo Fisher Scientific). The membrane samples were applied under attenuated total reflectance (ATR)

mode. X-ray diffraction (XRD) patterns of samples were collected on a SmartLab X-ray diffractometer (Rigaku Corporation) with 2θ ranging from 0.5° to 40° and a scanning rate of $1.2^\circ \text{ min}^{-1}$ at room temperature. The morphologies of the COF nanofibers and membranes were observed by field-emission scanning electron microscopy (SEM, S-4800, Hitachi) operated at 5 kV. All samples were ion-sputtered with platinum prior to imaging. Transmission electron microscope (TEM) images were obtained with a Tecnai 12 (FEI) microscope operated at 120 kV. Sample was prepared by drop-casting dispersion onto a carbon-coated copper grid. The surface topographies of the membranes were examined by atomic force microscopy (AFM, XE-100, Park Systems), and the scanning rate was 0.5 Hz. The water contact angle (WCA) measurements were conducted on a contact angle goniometer (Drop Meter A100P, MAIST). The surface charges of membranes were analyzed using an electrokinetic analyzer (SurPASS, Anton Paar GmbH) with a streaming potential method. A 0.1 mmol L^{-1} KCl solution was used as the background electrolyte solution, and the pH values were adjusted by 0.1 mol L^{-1} NaOH and HCl solutions, respectively.

Nanofiltration performance evaluation. The nanofiltration performance was tested on a lab-scale cross-flow filtration system consisted of three membrane test cells in parallel. The effective membrane area was 7.1 cm^2 . The operating pressure was applied at 4 bar, and the feed flow rate was 30 L h^{-1} . The concentration of all inorganic salts solutions was 1000 ppm. All membranes were pre-compacted under 5 bar for 1 h to reach stable flux, and the solution temperature was controlled by a heat exchanger at 25°C . The permeation flux (J , $\text{L m}^{-2} \text{ h}^{-1}$) and permeance (P , $\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) were calculated by the following equations:

$$J = \Delta V / (A \Delta t) \quad (1)$$

$$P = J / \Delta P \quad (2)$$

where ΔV (L) is the volume of the permeated solution, A (m^2) is the effective membrane area, Δt (h) is the filtration time, and ΔP (bar) is the applied pressure of filtration test.

The salt rejection rate was calculated as follows:

$$R = (1 - C_p / C_f) \times 100\% \quad (3)$$

where C_p and C_f are the concentrations of the permeated and feed solutions, respectively. The concentrations of solutions were measured using an electrical conductivity meter (S230-K, Mettler-Toledo)

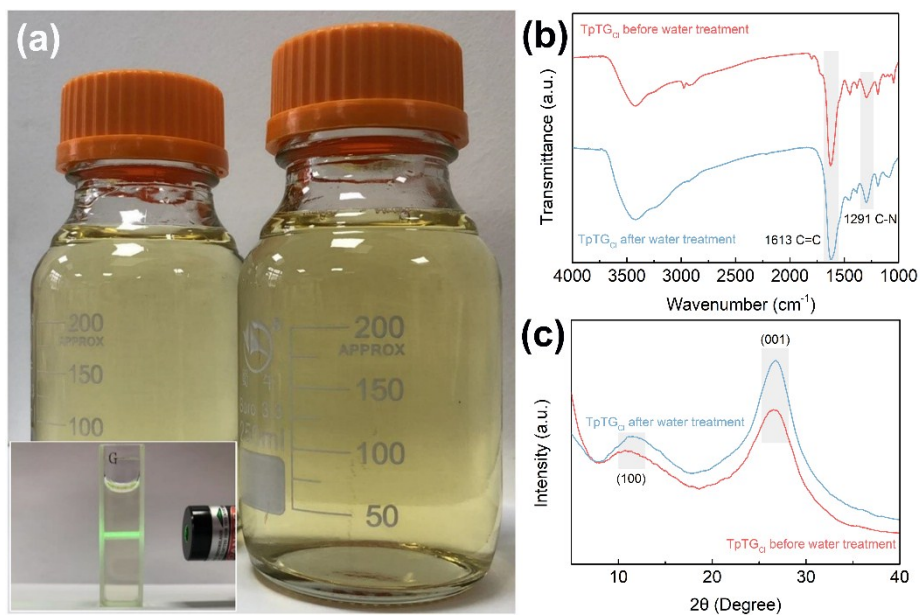


Fig. S2 Stability of TpTG_{Cl} nanofibers. (a) Digital image of TpTG_{Cl} dispersion (inset shows a typical Tyndall effect). (b) FTIR spectra of the TpTG_{Cl} nanofibers before and after water treatment (Soaking in water for 3 days). (c) XRD patterns of the TpTG_{Cl} nanofibers before and after water treatment (Soaking in water for 3 days).

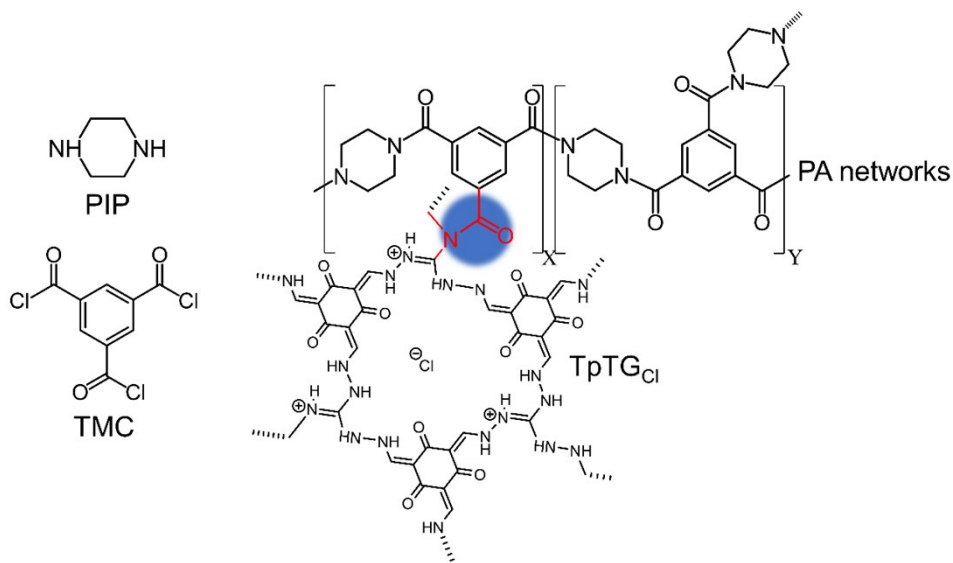


Fig. S3 Schematic diagram of the possible reaction between TpTG_{Cl} and PA networks during IP process.

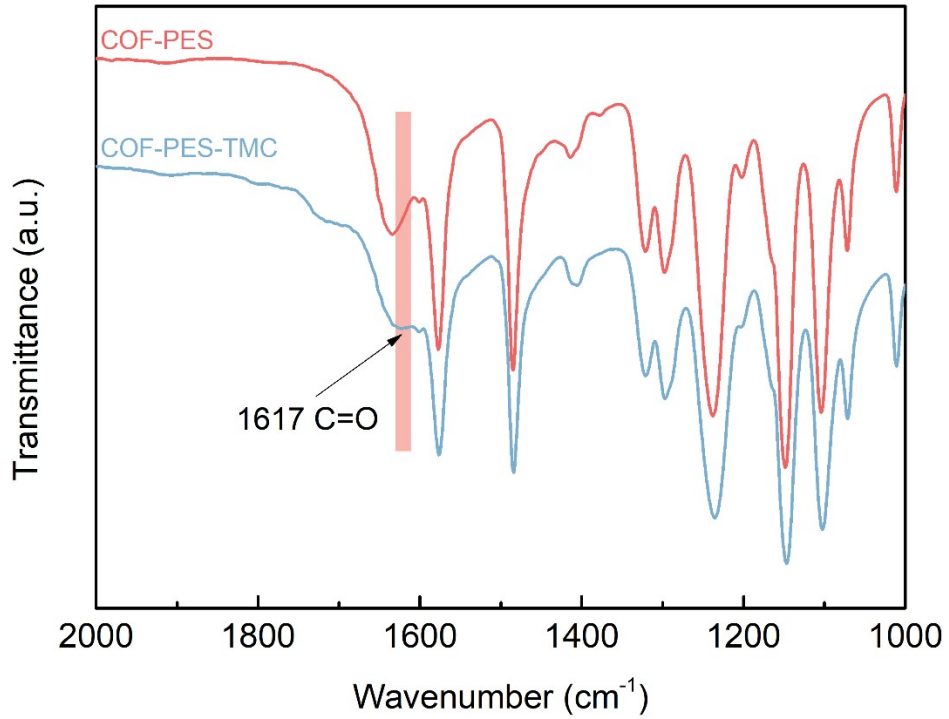


Fig. S4 FTIR spectra of COF-deposited PES substrate before (COF-PES) and after (COF-PES-TMC) TMC treatment.

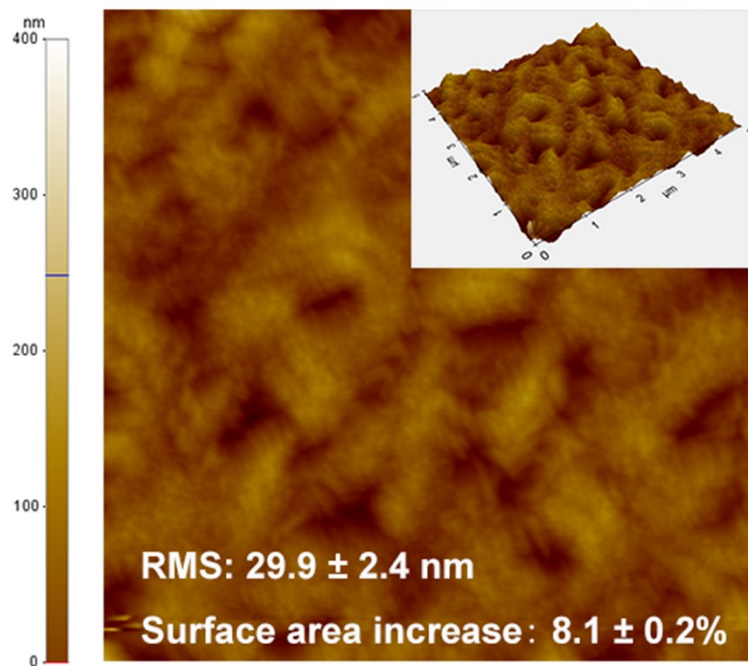


Fig. S5 AFM topography images of control membrane (scanning area was $5 \mu\text{m} \otimes 5 \mu\text{m}$).

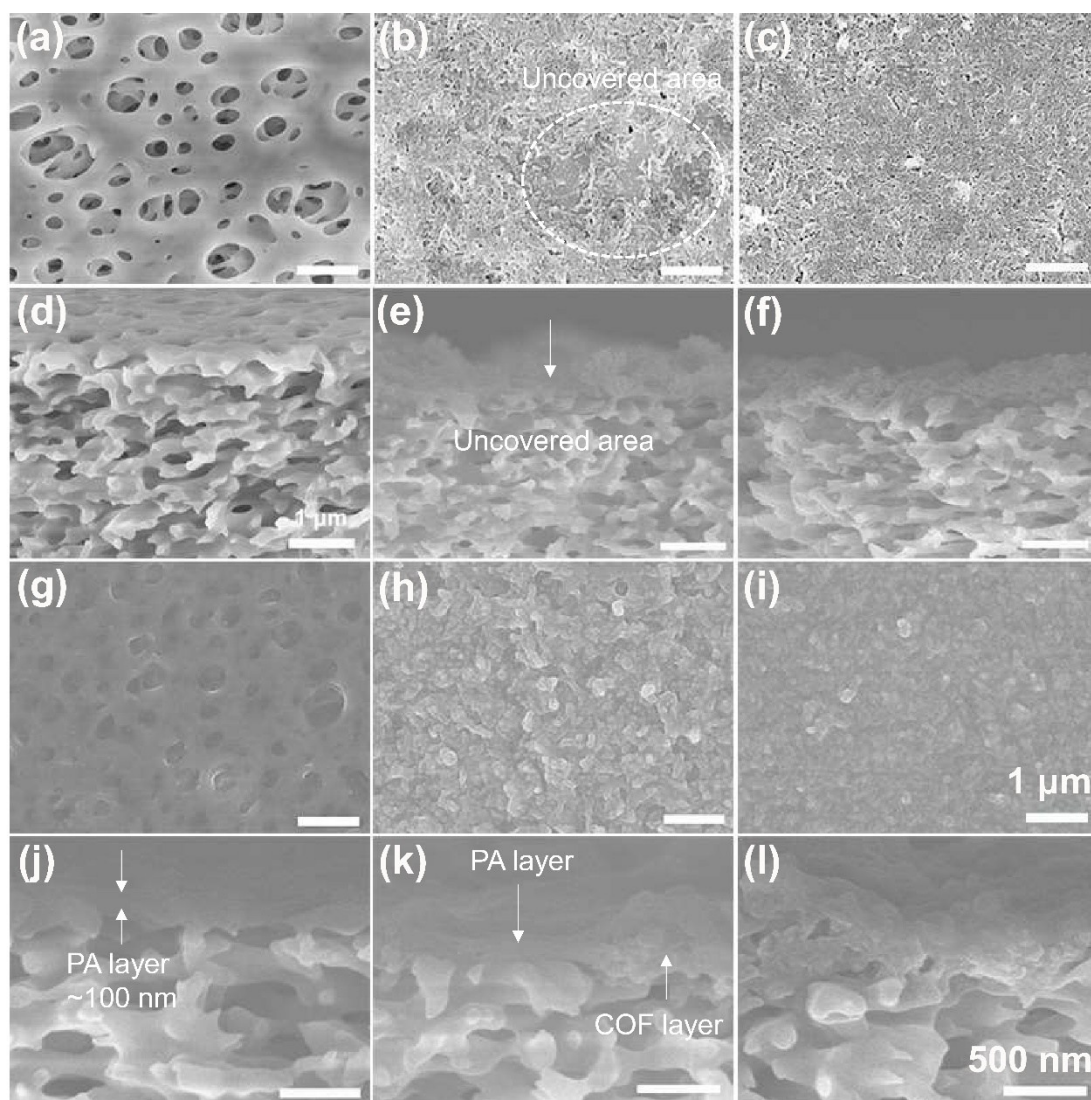


Fig. S6 Surface and cross-sectional SEM images with TpTG_{Cl} nanofiber deposition density of 0 mg cm⁻²: before (a,d) and after (g,j) IP. Surface and cross-sectional SEM images with TpTG_{Cl} nanofiber deposition density of 0.019 mg cm⁻²: before (b,e) and after (h,k) IP. Surface and cross-sectional SEM images with TpTG_{Cl} nanofiber deposition density of 0.051 mg cm⁻²: before (c,f) and after (i,l) IP. (The scale bars in Fig. S6a-i are 1 μm. The scale bars in Fig. S6j-l are 500 nm)

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